the product of the concentrations of all three substances. Without making assumptions, the truth of which cannot at present be verified, it is impossible to represent the reaction by means of a chemical equation, in which the change takes place between three molecules only. Like many other reactions, it is of a lower order than would be the case if the order were determined by the number of molecules represent ed by the chemical equation as taking part in it. The cause of this simplicity remains at present unknown. The influence of temperature on the velocity of change is well represented by Van 't Hoff's well-known equation ("Études," p. 115). An increase of temperature from 0° to 10° C. increases the velocity 2·7 times; all other reactions, so far studied, are influenced to much the same extent, the effect of a rise of temperature of 10° being to increase the velocity from 2 to 3·6 times; the average number is 2·8.

THE additions to the Zoological Society's Gardens during the past week include two Californian Quails (*Callipepla californica*, ♂ ♀) from California, presented by Mr. T. M. Howells; a Black-headed Lemur (*Lemur brunneus*), a Madagascar Boa (*Boa madagascariensis*) from Madagascar, a Canarian Pigeon (*Columba laurivora*) from the Canary Islands, deposited; two Black-necked Storks (*Xenorhynchus australis*) from Malacca, two Larger Tree Ducks (*Dendrocygna major*) from India, a Ruddy Sheldrake (*Tadorna casarca*, ♂), four Tufted Ducks (*Fuligula cristata*), European, purchased.

## OUR ASTRONOMICAL COLUMN.

MR. ISAAC ROBERTS ON LONG-EXPOSURE PHOTOGRAPHS.—In the current number of *Knowledge*, Mr. Isaac Roberts describes a beautiful photograph of Orion, taken by him with an exposure of seven hours thirty-five minutes, the photograph "depicting very probably the maximum of extent and detail that can be shown by aid of photographic methods." This statement, coming from one so versed in celestial photography, cannot be considered lightly, but must be carefully weighed before judgment be given. The reasons which Dr. Roberts gives for this statement are as follows: (1) The film of the negative is, in consequence of prolonged exposure to the latent sky luminosity, darkened on development to a degree that would obscure faint nebulosity and faint stars. (2) Longer exposures of the plates would not reveal additional details of nebulosity, nor more faint star images. Dr. Roberts goes on to say that, although he has taken all precautions to protect the plates from extraneous light, to photograph only on clear evenings, &c., yet the longer the exposure the darker the film becomes in the development of the images. The sequence, he states further, has been observed for many years on all very sensitive films which have had long exposure, and the results have been practically invariable. An important point, favouring Dr. Roberts' statement, is that the unexposed margins of the films do not undergo this process of being darkened, but remain perfectly clear. The point raised by him is one well worth consideration in these days of long exposures; and although the evidence he brings together is strong, yet we hope he has not proved his case.

VANADIUM IN SCANDINAVIAN RUTILE.—For producing the spectrum of titanium, Prof. B. Hasselberg used titanic acid in the form of rutile in the electric arc, finding that it was more suitable than commercial titanium. This rutile came from Krageröe, in Norway, its other chief component, besides titanic acid, being oxide of iron, in a quantity of about 1 or 2 per cent. The spectrum obtained from this substance, after the elimination of known impurities, was thought at first to be pure titanium, but it was found "that among the fainter and faintest lines of my titanium spectrum there are several that doubtless belong to *vanadium*." A re-examination of a large piece of the latter, and subsequent comparison photographs of vanadium and rutile, exhibited many striking similarities. Another kind of rutile was put to the same test. This was Swedish rutile from Käringbricka, in Westmanland, which contained chromium in addition. A comparison photograph of the spectra showed hat the same series of coincidences was found as in the case of the Norwegian rutile, as Prof. Hasselberg shows in the table of his results, given in the *Astrophysical Journal* for March (No. 3). Further spectroscopic experiments suggested that the Swedish variety contained a greater amount of vanadium than the Norwegian; but whether the difference is sufficient to be recognised, or determined quantitatively chemically, remains uncertain.

COLUMBIA UNIVERSITY OBSERVATORY'S PUBLICATIONS.—In the two numbers (10 and 11) of the Contributions of this Observatory, Prof. Harold Jacoby presents two communications on (1) the reduction of stellar photographs with special reference to the Astro-photographic Catalogue plates, and (2) on the permanence of the Rutherfurd photographic plates. The first paper has been written at the request of Dr. Gill, who asked him to put together the formulæ which seemed best for the reduction of the Astro-photographic Catalogue plates. Prof. Jacoby acknowledges the work of others on the subject, and the method he gives is suitable for the reduction of any photographic plates, whether the programme of the Permanent Committee has been adopted or not. The only restrictions are that the centre of the plate must be more than 15° from the pole, and that the plate does not cover more than two square degrees. A description of the method would be too long to give here, so we will confine ourselves to the statement that Prof. Jacoby's formulæ greatly facilitate the computation as a whole. As an illustration of the method of reduction, he gives a fully worked-out example of a plate taken at Paris in 1891, and discussed by M. Prosper Henry. The second communication, dealing with the permanence of the Rutherfurd plates, gives the results of a comparison of the old measures of the Pleiades and those quite recently completed. The object of the investigation was to test the durability of the photographic film, and see whether any deformation, either contraction or expansion, had occurred in the interval since the first measurement, made nearly a quarter of a century ago. The question is one of great importance, since some of Rutherfurd's photographs are still unmeasured; it has, further, a great bearing on the plates of the astro-photographic chart of the heavens. The result of the investigation can be best illustrated by extracting from the final table the figures representing the differences between the old and new measures as obtained from three separate plates. These are as follows:—

*Rutherfurd Measures minus New Measures.*

| Star. | Plate 16. | | Plate 18. | | Plate 22. | |
|---|---|---|---|---|---|---|
| | Angle. | Dist. | Angle. | Dist. | Angle. | Dist. |
| | ″ | ″ | ″ | ″ | ″ | ″ |
| A 34 | 0·00 | −0·12 | −0·24 | −0·21 | +0·07 | +0·26 |
| 18*m* | − ·06 | − ·06 | + ·12 | + ·05 | − ·08 | − ·34 |
| A 12 | − ·01 | − ·18 | + ·40 | + ·14 | + ·16 | − ·10 |
| A 22 | − ·04 | + ·27 | − ·06 | − ·08 | − ·06 | + ·19 |
| A 24 | − ·02 | + ·16 | ·00 | + ·30 | − ·13 | + ·10 |
| A 28 | + ·08 | − ·10 | + ·18 | − ·13 | − ·12 | − ·13 |
| A 30 | − ·02 | − ·01 | − ·45 | + ·08 | + ·17 | − ·01 |
| A 39 | + ·41 | + ·03 | + ·14 | − ·18 | + ·39 | + ·02 |

The conclusions that can be drawn from the whole discussion are that the positions of the individual stars on the plates may be practically determined from either set of measures, the mean error amounting to about 0″·1. Thus the new measures will furnish practically identical results with those that would have been obtained if the plates had been measured twenty years earlier.

## A GIFT TO THE PARIS ACADEMY OF SCIENCES.

THE Paris correspondent of the *Times*, writing under date April 5, makes the following announcement:—

M. Berthelot read this afternoon, at the Academy of Sciences, the following letter addressed to him in French by Mr. H. Wilde,



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president of the Manchester Literary and Philosophical Society, announcing to the Academy the gift of 5500*l.* to be set apart for an annual prize of 4000f. I send you the original letter, without undertaking, considering its special and technical character, to translate it :—

Diverses considérations m'engagent actuellement à me mettre en communication avec l'Académie dans le but de stimuler de nouvelles investigations dans les sciences physico-chimiques, et de faire disparaître quelques-uns des obstacles qui entravent leurs progrès. L'un de ces obstacles qui appelle la sérieuse attention des penseurs philosophes est l'invasion d'une autorité dogmatique dans une science scolastique, pour soutenir des erreurs démontrées et des méthodes erronées d'observation et d'expérience. Il sera suffisant pour l'objet que j'ai actuellement en vue de citer le système périodique des éléments chimiques comme un exemple de l'abus d'autorité dans une branche de la science où vous occupez un rang si distingué. J'ai à vous exprimer mes regrets que vos vues au sujet de la prétendue loi périodique ne soient venues que récemment à ma connaissance ; sans cela je m'y serais référé dans mes travaux généraux sur les relations numériques des poids atomiques. Quoique vous ayez clairement indiqué, monsieur, dans vos "Origines de l'Alchimie," les sophismes et les contradictions inhérents à ce système, et que vous ayez également montré que la prédiction de l'existence et des propriétés des éléments inconnus n'a aucune relation nécessaire avec la prétendue loi périodique, cependant ce système a depuis été imposé aux personnes qui s'occupent de science par les sociétés scientifiques et les corps enseignants comme une vérité natureile d'une autorité indiscutable.

Je n'ai pas besoin de vous rappeler que l'état actuel de la chimie théorique en raison de la connaissance formelle de ce dogme est réellement déplorable. Les savants qui aspirent à se distinguer dans la chimie et dans la physique estiment qu'il est nécessaire de donner des preuves de leur croyance personnelle, en tâchant de montrer la correlation de leurs propres travaux sur des points particuliers avec le système périodique, et ils évitent toute référence aux proportions multiples des poids atomiques, comme à une dangereuse hérésie. Beaucoup de ces néophytes, de même que certains auteurs de manuels, ne peuvent se fair une idée, ou ignorent la signification de l'idée de la périodicité telle qu'elle est définie par De Chancourtois, Newlands et Mendeleief dans leurs mémoires respectifs. Ils appliquent l'expression impropre de loi périodique à la progression de propriétés antérieurement commes observables dans les familles naturelles des éléments, à la correlation avec les poids atomiques de propriétés physiques et chimiques établies depuis longtemps, à la progression bien connue des propriétés physiques dans les séries homologues des composés organiques. Par suite, le danger pour les progrès futurs de la chimie théorique est que, lorsque l'idée illusoire d'une spiro-périodicité des propriétés analogues des éléments sera universellement abandonnée, le nom impropre de loi périodique est exposé à prendre dans la science un caractère narasite de la même facon que cette autre expression impropre, "esprit lunatique," avec ses dérivés, subsiste encore dans la civilisation moderne comme une survivance de la physiologie mentale barbare des âges passés.

Heureusement pour l'avenir de la philosophie chimique que l'esprit de Dumas vit encore dans les esprits de la plupart des chimistes français, qui ne reconnaissent aucune autre autorité que la vérité de la nature telle qu'elle se présente à l'entendement, et qu'ils sont par là exempts de l'illusion de la prétendue loi périodique. En reconnaissance des nombreux profits que j'ai retirés de la science française, tant pure qu'appliquée, j'ai l'honneur d'offrir à l'Académie la somme de 5500*l.* (137,500f.) pour être placée en rente française, et l'intérêt provenant de cette somme devra être appliqué à la fondation d'un prix de 4000f. à décerner tous les ans à l'auteur d'une découverte ou d'un ouvrage quelconque en astronomie, physique, chimie, minéralogie, géologie, et mécanique, qui, au jugement de l'Académie, sera jugé le plus méritant. L'attribution de ce prix sera internationale et pourra être retrospective.

Alderley Edge, Cheshire, 15 Mars, 1897.

The gift has given great satisfaction at the Academy, and is as much to the honour of the donor as to that of the distinguished secretary of that Academy, whose work is referred to in such terms of gratitude.

## *THE THEORY OF OSMOTIC PRESSURE.*[1]

AS osmotic theory is now attracting general attention in this country, it seems desirable that all the positions that are maintained in regard to it should be clearly set forth. The excuse for offering the following remarks is that for some time I have paid attention to the subject in its relations to general molecular theory, both in the thermal and the electrical aspects. I fail to recognise how the validity of the thermodynamic basis of the law of osmotic pressure can be shaken ; and though the idea of ionic dissociation in solutions is an additional hypothesis which must be judged separately by the extent of its agreement with the facts, it appears to me that in some form—possibly not at all in the chemical imagery with which it is at present often associated—it holds the field. It is difficult, in fact, to see how the hypothesis that the same chemical element can have different valencies in different series of compounds, which is now usually accepted, is fundamentally any whit less parodoxical than the hypothesis of ionic dissociation ; anything that throws light on the one must also illuminate the other.

In his recent note on this subject, Lord Kelvin[2] appears to allow, within certain limits, the cogency of the argument which bases the law of osmotic pressures on Henry's empirical law of solubility for gases ; an argument which has recently been carefully re-stated by Lord Rayleigh, having previously been employed, as he remarks, in forms more or less explicit, by van 't Hoff, Nernst, and other investigators. The connection thus established, however, hardly amounts to a physical demonstration, because it only deduces one empirical relation from another. Yet it seems desirable to draw attention to the fact, which I have not seen anywhere remarked, that this method had been employed by von Helmholtz in 1883, some time before van 't Hoff announced his theory of the correlation between osmotic and gaseous pressures ; and that the principles given by him in an investigation of the work-equivalent of gaseous solution, made in connection with the theory of galvanic polarisation,[3] involve in fact an implicit prediction of the osmotic law. This circumstance, that the law of osmotic pressure as regards dissolved gases is tacitly involved in von Helmholtz's equations, does not, of course, confer on him a position in the actual development of the subject.

But the theory of osmotic pressure can, I think, be placed on a purely abstract basis, independently of the law of solubility of gases, which would then assume the form of a deduction from it. The broad principles on which this is to be done have been in fact laid down, in a precise but very general manner, and without special applications, by Willard Gibbs as early as 1875, in his fundamental development of the laws of mechanical availability of energy.[4] The following position is, I believe, sound. Each molecule of the dissolved substance forms for itself a *nidus* in the solvent ; that is, it sensibly influences the molecules around it up to a certain minute distance, so as to form a loosely-connected complex, in the sense not of chemical union but of physical influence. The laws of this mutual molecular influence are unknown, possibly unknowable ; but provided the solution is so dilute that each such complex is, for very much the greater part of the time, out of range of the influence of the other complexes (as, for instance, are the separate molecules of a free gas), then the principles of thermodynamics necessitate the osmotic laws. It does not matter whether the nucleus of the complex is a single molecule, or a group of molecules, or the entity that is called an ion ; the pressure phenomena are determined merely by the number of complexes per unit volume.

To determine the osmotic forces, we must know the change in *available* energy that is involved in dilution of the solution by further transpiration of the pure solvent into it. In finding that change, the laws of mutual action between molecules of the dissolved substance are not required ; for there is actually no action between them, and as soon as the solution becomes so concentrated that such mutual action between the complexes comes in, the theory is no longer exact. Nor are the laws of mutual action between the molecules of the dissolved substance and

[1] Read before the Cambridge Philosophical Society, January 25, by J. Larmor, F.R.S.

[2] *Proc.* R.S. Edin., January ; NATURE, January 21, p. 272.

[3] H. von Helmholtz, "Zur Thermodynamik Chemischer Vorgänge, iii." in Collected Papers, vol. iii. pp. 105–114, especially his equation (4) and the theory of diffusion at the end. [The theory had already been given explicitly in 1876 by Willard Gibbs, *loc. cit. infra*, p. 227.]

[4] *Trans.* Connecticut Academy, November 1875, p. 138 : "Effect of a Diaphragm Equilibrium of Osmotic Forces)."



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